

# (11) **EP 2 432 744 B1**

# (12)

# **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:

15.07.2020 Bulletin 2020/29

(21) Application number: 10724205.9

(22) Date of filing: 21.05.2010

(51) Int CI.:

(86) International application number: PCT/US2010/035705

(87) International publication number: WO 2010/135614 (25.11.2010 Gazette 2010/47)

# (54) THIN SUBSTRATES HAVING MECHANICALLY DURABLE EDGES

DÜNNE SUBSTRATE MIT MECHANISCH WIDERSTANDSFÄHIGEN KANTEN SUBSTRATS MINCES AYANT DES BORDS MÉCANIQUEMENT DURABLES

(84) Designated Contracting States:

AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO SE SI SK SM TR

- (30) Priority: 21.05.2009 US 180230 P
- (43) Date of publication of application: **28.03.2012 Bulletin 2012/13**
- (73) Proprietor: Corning Inc. Corning, NY 14831 (US)
- (72) Inventors:
  - GARNER, Sean M.
     Elmira, New York 14905 (US)

- GLAESEMANN, Gregory S.
   Corning, New York 14830 (US)
- LI, Xinghua Horseheads, New York 14845 (US)
- (74) Representative: Elkington and Fife LLP Prospect House 8 Pembroke Road Sevenoaks, Kent TN13 1XR (GB)
- (56) References cited:

EP-A1- 1 803 601 WO-A1-2007/140978
DE-A1- 19 810 325 US-A- 6 120 908
US-A1- 2006 021 385 US-B1- 6 407 360
US-B1- 6 815 070

P 2 432 744 B1

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

# Description

10

35

#### **BACKGROUND**

[0001] Glass substrates are currently being used as protective covers or windows for display and touch sensor devices, as well as substrates for front and back planes of electronic devices. As such, these substrates are susceptible to mechanical failure originating at flaws at the edges of the substrate. Such flaws are either created during the cutting and edge finishing process or from contact damage occurring during handling and use.

**[0002]** Edge finishing, which includes grinding, polishing, and/or etching of the edges of the substrate, attempts to eliminate major flaws that are generated during the cutting process and minimize chipping due to contact damage. In addition, such finishing processes have been focused on preventing damage due to edge impact from point sources. Finishing processes are generally capable of removing flaws generated during scribe and breaking processes and produce edge shapes that are more tolerant of edge impact. However, these finishing processes produce lower edge strength than is achievable. In addition, it is difficult to use such finishing processes when the substrate thickness is below about 0.3 mm. Due to the reduced contact area, substrates having thicknesses in this range are susceptible to breakage during edge impact, whether or not they have been edge finished.

US 6,815,070 B1 discloses a glass-plastic composite film.

DE 19810 325 A1 discloses a method for increasing the edge strength of a thin glass sheet.

WO 2007/140978 A1 discloses a method in which a glass pane is surrounded by a covering at least in sections.

US 6,120,908 discloses a method in which an oxide substrate is coated with a strengthening composition.

# **SUMMARY**

**[0003]** In a first aspect, a substrate comprising a sheet of either a glass, a glass ceramic, or a ceramic and having increased edge strength is provided as set out in claim 1. In a second aspect, a method of making the substrate is provided, as set out in claim 9.

[0004] In one embodiment, the substrate has a thickness of up to about 0.6 mm.

**[0005]** In another embodiment, the substrate has a thickness of up to about 0.1 mm.

[0006] In another embodiment, the polymeric edge coating has a modulus of up to about 10 GPa.

[0007] In another embodiment, each of the at least two parallel high strength edges is slot-drawn, fusion-drawn, redrawn, or laser cut.

**[0008]** In another embodiment, substrate comprises one of a borosilicate glass, an aluminoborosilicate glass, and an alkali aluminosilicate glass.

**[0009]** In a further embodiment, the alkali aluminosilicate glass comprises: 60-70 mol% SiO<sub>2</sub>; 6-14 mol% Al<sub>2</sub>O<sub>3</sub>; 0-15 mol% B<sub>2</sub>O<sub>3</sub>; 0-15 mol% Li<sub>2</sub>O; 0-20 mol% Na<sub>2</sub>O; 0-10 mol% K<sub>2</sub>O; 0-8 mol% MgO; 0-10 mol% CaO; 0-5 mol% ZrO<sub>2</sub>; 0-1 mol% SnO<sub>2</sub>; 0-1 mol% CeO<sub>2</sub>; less than 50 ppm As<sub>2</sub>O<sub>3</sub>; and less than 50 ppm Sb<sub>2</sub>O<sub>3</sub>; wherein 12 mol%  $\leq$  Li<sub>2</sub>O + Na<sub>2</sub>O + K<sub>2</sub>O  $\leq$  20 mol% and 0 mol%  $\leq$  MgO + CaO  $\leq$  10 mol%.

 $\begin{tabular}{l} \textbf{[0010]} & In a further embodiment, the alkali aluminosilicate glass comprises: $64$ mol% $\leq $SiO_2$ $\leq $68$ mol%; $12$ mol% $\leq $Na_2O$ $\leq $16$ mol%; $8$ mol%; $2$ mol%; $0$ mol%; $0$ mol%; $2$ mol%; $2$ mol%; $2$ mol%; $4$ mol%; $4$ mol% $\leq $MgO$ $\leq $6$ mol%; and $0$ mol% $\leq $CaO$ $\leq $5$ mol%, wherein: $66$ mol% $\leq $SiO_2$ + $B_2O_3$ + $CaO$ $\leq $69$ mol%; $Na_2O$ + $K_2O$ + $B_2O_3$ + $MgO$ + $CaO$ + $SrO$ $\geq $8$ mol%; $(Na_2O$ + $B_2O_3$) - $Al_2O_3$ $\leq $2$ mol%; $2$ mol% $\leq $Na_2O$ - $Al_2O_3$ $\leq $6$ mol%; and $4$ mol% $\leq $(Na_2O$ + $K_2O$) - $Al_2O_3$ $\leq $10$ mol%, and wherein the glass has a liquidus viscosity of at least $130$ kpoise. } \end{tabular}$ 

**[0011]** In a further embodiment, the alkali aluminosilicate glass comprises: 50-80 wt%  $SiO_2$ ; 2-20 wt%  $Al_2O_3$ ; 0-15 wt%  $B_2O_3$ ; 1-20 wt%  $Na_2O$ ; 0-10 wt%  $Li_2O$ ; 0-10 wt%  $K_2O$ ; and 0-5 wt% (MgO + CaO + SrO + BaO); 0-3 wt% (SrO + BaO); and 0-5 wt% ( $ZrO_2 + TiO_2$ ), wherein  $0 \le (Li_2O + K_2O)/Na_2O \le 0.5$ .

**[0012]** In another embodiment, the substrate has at least one strengthened surface layer extending from at least one of the first surface and the second surface to a depth of layer, wherein the strengthened surface layer is under a compressive stress.

50 [0013] In a further embodiment, the strengthened surface layer is an ion-exchanged layer.

**[0014]** In another embodiment, the substrate further comprises at least one layer deposited on at least one of the first surface and the second surface.

**[0015]** In another embodiment, the substrate is a protective cover glass for at least one of a hand held electronic device, an information-related terminal, and a touch sensor device.

**[0016]** In an embodiment of the method, In an embodiment of the method, the step of providing the sheet comprises forming a sheet by one of fusion-drawing, slot-drawing, and redrawing.

**[0017]** In an embodiment of the method the step of providing the sheet comprises laser cutting the sheet to form the at least two parallel high strength edges.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

#### [0018]

20

30

35

50

55

FIGURES 1 and 3 are schematic representations of side views of the substrates showing typical edge profile designs in accordance with the invention and FIGURES 2 and 4, show designs not in accordance with an embodiment of the invention;

FIGURE 5 is an optical micrograph of and edge of a glass substrate;

FIGURES 6-9 are optical micrographs of laser-cut edges; and

FIGURE 10 is a Weibull plot of failure probabilities obtained for sample sets that were strength tested using a fourpoint bending test.

#### **DETAILED DESCRIPTION**

**[0019]** In the following description, like reference characters designate like or corresponding parts throughout the several views shown in the figures. It is also understood that, unless otherwise specified, terms such as "top," "bottom," "outward," "inward," and the like are words of convenience and are not to be construed as limiting terms. In addition, whenever a group is described as comprising at least one of a group of elements and combinations thereof, it is understood that the group may comprise, consist essentially of, or consist of any number of those elements recited, either individually or in combination with each other. Similarly, whenever a group is described as consisting of at least one of a group of elements or combinations thereof, it is understood that the group may consist of any number of those elements recited, either individually or in combination with each other. Unless otherwise specified, a range of values, when recited, includes both the upper and lower limits of the range, as well as any sub-ranges therebetween.

**[0020]** Referring to the drawings in general and to FIGS. land 3 in particular, it will be understood that the illustrations are for the purpose of describing particular embodiments and are not intended to limit the disclosure or appended claims thereto. The drawings are not necessarily to scale, and certain features and certain views of the drawings may be shown exaggerated in scale or in schematic in the interest of clarity and conciseness.

**[0021]** Glass substrates are currently being used as protective covers for display and touch applications, such as, but not limited to, portable communication and entertainment devices such as telephones, music players, video players, or the like; and as display screens for information-related terminals (IT) (e.g., portable or laptop computers) devices; as well as in other applications, such as electronic paper front plane and back plane substrates. Such glass substrates are susceptible to mechanical failures and breakage originating from edge flaws that are created either during the cutting and edge finishing process or from contact damage during handling, device fabrication, and use.

[0022] A substrate having increased edge strength is provided by eliminating the creation of strength limiting defects along the edges of the substrate and preserving the bend strength of the edge. The substrate comprises a sheet of either a glass, a glass ceramic, or a ceramic. Although the substrate may be referred to herein solely as a glass substrate, it is understood that the description is, unless otherwise specified, equally applicable to glass ceramic and ceramic materials, as well as multi-layer structures comprising discrete glass, glass-ceramic, and ceramic compositions. The sheet has a first surface, a second surface, and at least two parallel high strength edges joining the first and second surfaces. In one embodiment, the sheet may further include a polymeric coating on the first surface, second surface, or both. Each of the two parallel high strength edges has a bend strength that is capable of less than about 2% failure probability at a stress level of 200 MPa over a test length of 50 mm. An edge coating of a polymeric material covers at least a portion of each of the high strength edges, preserving the high strength edges from subsequent damage and preventing contamination of the edge. For example, once applied to the edge coating prevents crack systems from forming on the edge. In those embodiments in which a surface coating is present, the surface coating and edge coating can have compositions that are different from each other, and may be applied to the substrate at different times and by different processes.

**[0023]** In one embodiment, the substrate has a thickness of up to about 0.6 mm and, in another embodiment, has a thickness of up to about 0.4 mm. The substrate, in a third embodiment, has a thickness of up to about 0.1 mm. Due to their reduced contact area, substrates having thicknesses less than or equal to about 0.1 mm are particularly susceptible to breakage during edge impact, whether or not they have finished edges. Moreover, edge finishing using techniques such as polishing and the like are either ineffective or have not been demonstrated at thicknesses less than or equal to about 0.1 mm. It is therefore better to rely on a forming process and/or a cutting process that yields a high strength edge rather than use a finishing process to average the edge strength to a lower, uniform value.

**[0024]** In one embodiment, the at least two parallel high strength edges are created directly by a forming process. Such forming processes typically involve heating the glass to a temperature above the anneal point (i.e., the temperature at which the viscosity  $\eta$  of a glass equals  $10^{13}$  Poise; also referred to as the anneal temperature). Non-limiting examples of such forming processes include down-draw processes. Such down-draw processes are known in the art and include

slot-draw processes, fusion-draw processes, re-draw processes, and the like.

10

30

35

50

[0025] Alternatively, the high strength edges may be created by high strength cutting methods that include, but are not limited to, laser cutting techniques. Such laser cutting techniques include full-body laser separation using a CO2 laser having a wavelength of 10.6 μm. In CO<sub>2</sub> full body laser cutting, a glass substrate is heated to a temperature that is near (i.e., ± 50°C) the strain point of the glass to create a vent. Although the laser cutting of a glass substrate is described herein, it is understood that the laser cutting methods described herein may be used to cut or separate the other types of substrates (e.g., ceramics, glass ceramics) described herein). In one embodiment, the glass is then rapidly quenched - typically with a water jet - after heating by the laser. Quenching produces a tensile force over the glass vent, opening the vent in the direction of the relative motion of the glass substrate. Quenching creates a tensile force on the side of the glass substrate irradiated by the laser (the laser side) that is strong enough to open up and propagate the vent in the glass. Since the tensile force on the laser side must be balanced over the thickness of the glass, a compressive force is generated on the side of the glass opposite the laser side (the back side), creating a bending momentum in the glass. Due to the bending momentum, edge quality is difficult to control. The laser-cut edge can behave differently, depending on whether tension is applied on the laser side or the back side of the glass substrate. Severe bending can induce fracture surface features that act as flaws and decrease the edge strength of the glass. The dominating fracture mode in samples having low edge strength are shear and twist defects or changes in fracture steps and planes that are known as "hackles." Low strength edges often fail due to the presence of twist hackles on the edge face. An optical micrograph of an edge 205 of a laser-cut glass substrate 200 having a twist hackle 210 is shown in FIG. 5. In FIG. 5, twist hackle 210 runs from the back side 202 (top right in FIG. 5) to the bottom left of the glass substrate 200.

[0026] High strength edges can be formed by CO<sub>2</sub> full body laser cutting by eliminating flaws such as twist hackles and the like. Such flaws can be eliminated in cutting regimes in which the temperature is balanced over the thickness of the substrate at suitable laser power densities. The median strength of such laser-cut edges is typically greater than about 400 MPa. The effect of laser power and distance between the laser beam and the quenching water jet are shown in FIGS. 3-9, which are optical micrographs of laser-cut edges. The laser power and distance between the laser and water jet used on the samples shown in FIGS. 6-9 are: a) FIG. 6: 26 W power, 14 mm distance; b) FIG. 7: 26 W power, 24 mm distance; c) FIG. 8: 35 W power, 14 mm distance; and d) FIG. 9: 35 W power, 24 mm distance. Hackles 310 were observed under the laser cutting conditions used in FIGS. 6-8, whereas the conditions used to cut the edge shown in FIG. 9 produced an edge that is free of any visible hackles or other flaws.

[0027] One non-limiting example of such full body  $\mathrm{CO}_2$  laser cutting or separation technique in which cutting parameters are optimized to eliminate hackles that lead to low strength edges is described in U.S. Patent Application No. 12/469794, by Sean M. Garner et al., entitled "Waterless  $\mathrm{CO}_2$  Laser Full-Body Cutting of Thin Glass Substrates," filed May 21, 2009, in which a method for cutting glass substrates with a  $\mathrm{CO}_2$  laser without using a water jet is described. An elongated  $\mathrm{CO}_2$  laser beam and thermal diffusion are used to achieve bulk heating of a glass substrate, and subsequent surface convection loss produces a tensile/compressive/tensile stress through the thickness of the glass. A second non-limiting example of laser cutting/separation techniques is described in United States Patent Application No. 12/388,935, by Anatoli A. Abramov et al., entitled "Method of Separating Strengthened Glass," filed on February 19, 2009, which describes full-body or complete cutting or separation of a strengthened glass sheet by initiating a flaw in the glass at a depth greater than that of the strengthened surface layer of the glass, and creating a vent by treating the glass with a laser to heat the glass to a temperature in a range from about 50°C below the strain point of the glass up to a temperature between the strain point and the anneal point of the glass, the vent extending from the flaw at a vent depth greater than that of the strengthened surface layer to at least partially separate the glass.. Other laser separation methods in which a partial vent or median crack is formed and final separation is achieved by scribing and breaking can also be used to provide a high strength edge to substrate 100.

[0028] FIGS. 1-4 are schematic representations of side views of the substrates described herein, showing typical edge profile designs with FIGS 2 and 4 being designs not in accordance with the invention. Substrate 100 has a first surface 102, a second surface 104, and at least two parallel high strength edges 110, 112, one of which is shown in FIGS. 1-4. In one embodiment, each of the at least two parallel high strength edges has a rectangular profile 110 (FIGS. 1). Rectangular edge profile 110, in one embodiment, is formed by a cutting process such as, but not limited to, the laser cutting in separation techniques described herein. In a second embodiment, each of the at least two parallel high strength edges has a rounded profile 112 (FIGS. 3). Rounded edge profile 112, in one embodiment, is formed by a slot-draw process. Edge profiles 110, 112 have edge faces that are substantially free of visible defects and thus have a bend strength that is greater than edges formed by mechanical polishing methods. Edges that are finished by chemical methods, such as edging of the like, produce rounded edge profiles having edge strengths that are also greater than those achieved by mechanical finishing. However, chemical etching processes can be incompatible with the substrate or structures that are fabricated on the substrate. Each of the high strength edges 110, 112 of substrate 100 has a bend strength, such as a four-point bend edge strength, capable of less than 2% failure probability at a stress level of 200 MPa over a test length of 50 mm.

[0029] At least a portion of the high strength edges are coated with edge coating 120 comprising a polymeric material

(FIGS. 1-4) such as, but not limited to, those flexible or elastic polymeric materials known in the art. In one embodiment, the polymeric material comprises at least one of a silicone, an epoxy, an acrylate, a urethane, and combinations thereof having a modulus of less than about 10 GPa. Non-limiting examples of polymeric materials include UV curable optical adhesives or optical cements such as those manufactured by Norland™ Optical Adhesives (NOA60. NOA61, NOA63, NOA65, NOA68, NOA68T, NOA71, NOA72, NOA73, NOA74, NOA75, NOA76, NOA78, NOA81, NOA81, NOA83H, NOA84, NOA88, NOA89), Dow Corning™ (Sylgard 184 and other thermally curing silicones), Dymax™, and others. In particular, non-limiting examples of such materials are described in U.S. Patent 3,986,997 by Howard A. Clark, entitled "Pigment-Free Coating Compositions," issued October 19, 1976, which describes acidic dispersions of colloidal silica and hydroxylated sesquisiloxane in an alcohol-water medium to provide abrasion resistant coatings.

**[0030]** Edge coating 120 of the polymeric material has a thickness in a range from about 5  $\mu$ m up to about 50  $\mu$ m, and can be applied by those methods known in the art, such as dipping, painting, spraying, dispensing from a die, or the like. If the substrate is used for device manufacturing or if a patterned layer is formed on the substrate, the edge coating can be applied to the substrate either before or after device processing. Edge coating 120 primarily serves a mechanical function, preserving the high bend strength of the as-formed or cut high strength edges by protecting the substrate edge from further damage. In some embodiments, edge coating 120 need not be transparent.

**[0031]** The at least two parallel high strength edges are unfinished; i.e., they are as-formed and not finished by mechanical or chemical means; i.e., they are neither ground nor etched. The combination of the at least two parallel high strength edges and edge coating 120 described herein does not require such finishing. Consequently, the number of process steps to make substrate 100 is decreased while overall substrate yield is increased.

**[0032]** As previously stated, edge coating 120 coats at least a portion of each high strength edge. In some examples not in accordance with the invention shown in FIGS. 2 and 4, edge coating additionally covers a portion of first and second surfaces 102, 104 adjacent to the high strength edge. However, in accordance with the invention substrate 100 does not have e protective coatings on first surface 102 and second surface 104.

**[0033]** In some instances, various coatings or films, such as strengthening, anti-scratch, anti-reflective, anti-glare coatings or films, or the like, such as those are known in the art, may be applied to at least one of first surface 102 and second surface 104 of substrate 100. Edge coating 120 need not have the same composition of such coatings, nor does edge coating 120 have to be applied at the same time as any other surface coating that may be present. For example, a coating may be applied to at least one of first surface 102 and second surface 104 immediately after substrate 100 is formed, whereas high strength edges can be cut into or otherwise formed on substrate 100 and edge coatings 120 applied to the high strength edges after a device is fabricated on substrate 120, or just before substrate 100 is incorporated into a device.

30

35

50

[0034] The substrate 100 comprises, consists essentially of, or consists of a glass, a glass ceramic material, or a ceramic material suitable for applications such as thin (i.e.,  $\leq$ 0.6 mm or, alternatively,  $\leq$  0.4 mm). The substrate can have either a single, multiple, or graded composition, such as that produced by chemical strengthening of glass by ion exchange and, in one embodiment, is rollable (i.e., a continuous sheet of the substrate can be rolled up) or bendable. Non-limiting examples of such glass ceramic and ceramic materials include  $\beta$ -spogamene,  $\beta$ -quartz, nepheline, and the like.

[0035] In some embodiments, the substrate 100 comprises, consists essentially of, or consists of one of a borosilicate glass, an aluminoborosilicate glass, and an alkali aluminosilicate glass. In one embodiment, the substrate is an alkali aluminosilicate glass comprising: 60-70 mol%  $SiO_2$ ; 6-14 mol%  $Al_2O_3$ ; 0-15 mol%  $B_2O_3$ ; 0-15 mol%  $Li_2O$ ; 0-20 mol%  $Na_2O$ ; 0-10 mol%  $K_2O$ ; 0-8 mol% MgO; 0-10 mol% CaO; 0-5 mol% CaO; 0-5 mol% CaO; 0-1 mo

**[0036]** In one particular embodiment, the alkali aluminosilicate glass has the composition:  $66.7 \text{ mol}\% \text{ SiO}_2$ ;  $10.5 \text{ mol}\% \text{ Al}_2\text{O}_3$ ;  $0.64 \text{ mol}\% \text{ B}_2\text{O}_3$ ;  $13.8 \text{ mol}\% \text{ Na}_2\text{O}$ ;  $2.06 \text{ mol}\% \text{ K}_2\text{O}$ ; 5.50 mol% MgO; 0.46 mol% CaO;  $0.01 \text{ mol}\% \text{ ZrO}_2$ ;  $0.34 \text{ mol}\% \text{ As}_2\text{O}_3$ ; and 0.007 mol% composition:  $66.4 \text{ mol}\% \text{ SiO}_2$ ;  $10.3 \text{ mol}\% \text{ Al}_2\text{O}_3$ ;  $0.60 \text{ mol}\% \text{ B}_2\text{O}_3$ ;  $4.0 \text{ mol}\% \text{ Na}_2\text{O}$ ;  $2.10 \text{ mol}\% \text{ K}_2\text{O}$ ; 2.76 mol% MgO; 2.576 mol% MgO;

**[0037]** The alkali aluminosilicate glass, in one embodiment, is down-drawable; i.e., formable by methods such as slot-draw or fusion-draw processes that are known in the art. In these instances, the glass has a liquidus viscosity of at least 130 kpoise. Non-limiting examples of such alkali aluminosilicate glasses are described in U.S. Patent Application No.

11/888,213, by Adam J. Ellison et al., entitled "Down-Drawable, Chemically Strengthened Glass for Cover Plate," filed on July 31, 2007, which claims priority from U.S. Provisional Patent Application 60/930,808, filed on May 22, 2007, and having the same title; U.S. Patent Application No. 12/277,573, by Matthew J. Dejneka et al., entitled "Glasses Having Improved Toughness and Scratch Resistance," filed on November 25, 2008, which claims priority from U.S. Provisional Patent Application 61/004,677, filed on November 29, 2007, and having the same title; U.S. Patent Application No. 12/392,577, by Matthew J. Dejneka et al., entitled "Fining Agents for Silicate Glasses," filed February 25, 2009, which claims priority from U.S. Provisional Patent Application No. 61/067,130, filed February 26, 2008, and having the same title; U.S. Patent Application No. 12/393,241 by Matthew J. Dejneka et al., entitled "Ion-Exchanged, Fast Cooled Glasses," filed February 26, 2009, which claims priority from U.S. Provisional Patent Application No. 61/067,732, filed February 29, 2008. and having the same title; and U.S. Provisional Patent Application No. 61/087324, by Kristen L. Barefoot et al., entitled "Chemically Tempered Cover Glass," filed August 8, 2008.

10

20

30

35

40

45

50

55

[0038] In one embodiment, substrate 100 comprises, consists essentially of, or consists of an alkali aluminosilicate glass that is either thermally or chemically strengthened. The strengthened alkali aluminosilicate glass has strengthened surface layers extending from first surface 102 and second surface 104 to a depth of layer below each surface. The strengthened surface layers are under compressive stress, whereas a central region of substrate 100 is under tension, or tensile stress, so as to balance forces within the glass. In thermal strengthening (also referred to herein as "thermal tempering"), substrate 100 is heated up to a temperature that is greater than the strain point of the glass but below the softening point of the glass and rapidly cooled to a temperature below the strain point to create strengthened layers at the surfaces of the glass. In another embodiment, substrate 100 can be strengthened chemically by a process known as ion exchange. In this process, ions in the surface layer of the glass are replaced by - or exchanged with - larger ions having the same valence or oxidation state. In one particular embodiment, the ions in the surface layer and the larger ions are monovalent alkali metal cations, such as Li<sup>+</sup> (when present in the glass), Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup>. Alternatively, monovalent cations in the surface layer may be replaced with monovalent cations other than alkali metal cations, such as Ag<sup>+</sup> or the like.

[0039] Ion exchange processes are typically carried out by immersing glass in a molten salt bath containing the larger ions to be exchanged with the smaller ions in the glass. It will be appreciated by those skilled in the art that parameters for the ion exchange process, including, but not limited to, bath composition and temperature, immersion time, the number of immersions of the glass in a salt bath (or baths), use of multiple salt baths, additional steps such as annealing, washing, and the like, are generally determined by the composition of the glass and the desired depth of layer and compressive stress of the glass as a result of the strengthening operation. By way of example, ion exchange of alkali metal-containing glasses may be achieved by immersion in at least one molten bath containing a salt such as, but not limited to, nitrates, sulfates, and chlorides of the larger alkali metal ion. The temperature of the molten salt bath typically is in a range from about 380°C up to about 450°C, while immersion times range from about 15 minutes up to about 16 hours. However, temperatures and immersion times different from those described above may also be used. Such ion exchange treatments typically result in strengthened alkali aluminosilicate glasses having depths of layer ranging from about 10  $\mu$ m up to at least 50  $\mu$ m with a compressive stress ranging from about 200 MPa up to about 800 MPa, and a central tension of less than about 100 MPa.

[0040] Non-limiting examples of ion exchange processes are provided in the U.S. patent applications and provisional patent applications that have been previously referenced hereinabove. In addition, non-limiting examples of ion exchange processes in which glass is immersed in multiple ion exchange baths, with washing and/or annealing steps between immersions, are described in U.S. Provisional Patent Application No. 61/079,995, by Douglas C. Allan et al., entitled "Glass with Compressive Surface for Consumer Applications," filed July 11, 2008, in which glass is strengthened by immersion in multiple, successive, ion exchange treatments in salt baths of different concentrations; and U.S. Provisional Patent Application No.61/084,398, by Christopher M. Lee et al., entitled "Dual Stage Ion Exchange for Chemical Strengthening of Glass," filed July 29, 2008, in which glass is strengthened by ion exchange in a first bath is diluted with an effluent ion, followed by immersion in a second bath having a smaller concentration of the effluent ion than the first bath. [0041] A method of making a substrate having increased edge strength, described hereinabove, is also provided. A sheet comprising at least one of a glass, glass ceramic, and a ceramic is first provided. The sheet has a first surface, a second surface, and at least two parallel high strength edges. As previously described herein, the at least two parallel high strength edges are, in one embodiment, created directly by a forming process, such as down-draw processes, fusion-draw processes, slot-draw processes, re-drawing processes, and the like, that involves heating the sheet to a temperature above the anneal point of the sheet. Alternatively, the high strength edges may be created by high strength cutting methods that include, but are not limited to, the laser cutting techniques described herein.

**[0042]** A polymeric edge coating is then deposited on at least a portion of each of the two parallel high strength edges to form the substrate. The polymeric edge coating, in one embodiment, has a modulus of less than about 10 GPa, and comprises a polymeric material, such as those described hereinabove. Each of the high strength edges of the substrate has a bend strength, such as a four-point bend edge strength, capable of less than 2% failure probability at a stress level of 200 MPa over a test length of 50 mm.

# Example

**[0043]** The following example illustrates some of the features and advantages of the substrate and methods described herein and is in no way intended to limit either the disclosure or the appended claims thereto.

**[0044]** The edge strength of fusion-drawn Corning EAGLE XG<sup>™</sup> aluminoborosilicate glass samples and full-body laser-cut edges, was tested using a four point bending test. Each sample tested had a length of 50 mm and a thickness of 0.63 mm. Testing of a given sample was stopped if a stress level of 280 MPa was reached without sample failure.

[0045] FIG. 10 is a Weibull plot of failure probabilities obtained for sets of samples having low strength edges (Data set 1 in Table 1 and groups 1 and 2 in FIG. 10), and having high strength laser-cut edges (Data set 2 and groups 3 and 4 in FIG. 10), as described herein. The samples classified as having low edge strength have full-body laser-cut edges that contain shear and twist defects and/or changes in fracture steps and/or planes that are known as "hackles" (see FIGS. 5-8). Such hackles lead to failure of the edge (FIG. 5). Although the high strength edges are also the product of full-body laser cutting, the laser cutting parameters (e.g., speed of translation of the laser and quenching streams (if present) along the surface of the glass substrate, distance between the laser and the quenching stream, etc.) have been optimized to eliminate hackles and other edge defects and thus produce a high strength edge (FIG. 4).

**[0046]** Edge strength testing was carried out up to a tensile stress of 280 MPa, The results of the edge strength testing are listed in Table 1, which lists the tensile stress at which individual samples failed. The term the "laser side," refers to the surface of the sample exposed to the laser during the laser-cutting process, whereas the "backside" refers to the side of the sample opposite the laser side. If a sample did not fail at a tensile stress less than or equal to 280 MPa, the sample was deemed to have "passed" the edge strength test, as noted by "pass" in Table 1.

Table 1. Results of edge strength testing

Sample No.	Tensile Stress (MPa) Data set 1		Tensile Stress (MPa) Data set 2		
	Backside	Laser Side	Backside	Laser Side	
1	153	244	Pass	Pass	
2	Pass	Pass	Pass	Pass	
3	208	Pass	Pass	Pass	
4	111	Pass	Pass	Pass	
5	91	Pass	257	Pass	
6	190	129	Pass	Pass	
7	Pass	Pass	Pass	Pass	
8	237	Pass	Pass	Pass	
9	172	Pass	Pass	Pass	
10	198	Pass	Pass	Pass	
11	Pass	Pass	Pass	Pass	
12	Pass	Pass	Pass	Pass	
13	Pass	Pass	Pass	Pass	
14	222	140	Pass	Pass	
15	223	Pass	Pass	Pass	
16	236	242	Pass	225	
17	Pass	Pass	Pass	Pass	
18	Pass	Pass	Pass	Pass	
19	223	Pass	Pass	Pass	
20	Pass	Pass	Pass	Pass	
21	Pass	Pass	Pass	Pass	
22	Pass	Pass	Pass	Pass	
23	Pass	Pass	Pass	Pass	
24	Pass	Pass	Pass	Pass	
25	Pass	170	226	Pass	
26	149	204	Pass	Pass	
27	92	Pass	Pass	224	
28	Pass	Pass			

(continued)

		Tensile Stress (MPa)		Tensile Stress (MPa)		
	Sample No.	Data	Data set 1		Data set 2	
5		Backside	Laser Side	Backside	Laser Side	
	29	203	Pass			
	30	239	Pass			
	31	218	Pass			
10	32	257	212			
	33	228	Pass			
	34	117	Pass			
	35	Pass	Pass			
	36	Pass	Pass			
15	37	251	Pass			
	38	Pass	Pass			
	39	Pass	Pass			
	40	211	Pass			
20	41	Pass	Pass			
	42	158	Pass			
	43	178	Pass			
	44	165	Pass			
	45	Pass	Pass			
25	46	Pass	Pass			
	47	131	Pass			
	48	Pass	Pass			
	49	Pass	Pass			
30	50		Pass			
	51		Pass			
	1	1			1	

[0047] For the samples having low strength edges, backside and laser side data sets (Data set 1 in Table 1 and groups 1 and 2 in FIG. 10) of about 50 samples each, the failure probability at a stress level of 200 MPa ranged from 5% to 30%. Backside and laser side data sets for samples having high strength edges (Data set 2 in Table 1 and groups 3 and 4 in FIG. 10), each consisted of 27 samples. For this combined number of 54 samples, no failures occurred at stress levels of less than 200 MPa, and only two samples in each set failed below 280 MPa. These results demonstrate the ability to create high strength edges capable of < 2% failure probability at a stress level of 200 MPa or greater.

[0048] While typical embodiments have been set forth for the purpose of illustration, various modifications, adaptations,

and alternatives may occur to one skilled in the art without departing from the scope of the appended claims.

#### Claims

35

40

45

50

55

1. A substrate (100), the substrate (100) comprising:

a. a sheet comprising at least one of a glass, a ceramic, and a glass ceramic, the sheet having a first surface (102), a second surface (104), and at least two parallel high strength edges joining the first surface (102) and the second surface (104), wherein each of the at least two parallel high strength edges has a bend strength capable of less than 2% failure probability at a stress level of 200 MPa over a test length of 50 mm; and b. a polymeric edge coating (120) covering at least a portion of each of the at least two parallel high strength edges, wherein the polymeric edge coating (120) has a thickness in a range from 5  $\mu$ m to 50  $\mu$ m and protects each of the at least two parallel high strength edges from the introduction of defects and damage,

characterised in that each of the at least two parallel high strength edges is unfinished; in that the first surface (102) of the sheet and the second surface (104) of the sheet are each entirely free of the polymeric edge coating (120); and in that the polymeric edge coating (120) comprises at least one of a silicone, an epoxy, an acrylate, a

urethane, and combinations thereof.

- 2. The substrate (100) according to Claim 1, wherein the substrate (100) has a thickness of up to 0.6 mm.
- 5 3. The substrate (100) according to Claim 2, wherein the substrate (100) has a thickness of up to 0.1 mm.
  - **4.** The substrate (100) according to any one of Claims 1-3, wherein the polymeric edge coating (120) has a modulus of up to 10 GPa.
- 5. The substrate (100) according to any one of Claims 1-4, wherein the substrate (100) has at least one strengthened surface layer extending from at least one of the first surface (102) and the second surface (104) to a depth of layer, wherein the strengthened surface layer is under a compressive stress.
  - 6. The substrate (100) according to Claim 5, wherein the strengthened surface layer is an ion-exchanged layer.
  - 7. The substrate (100) according to any one of Claims 1-6, further comprising at least one layer deposited on at least one of the first surface (102) and the second surface (104).
  - **8.** The substrate (100) according to any one of Claims 1-7, wherein the substrate (100) is a protective cover glass for at least one of a hand held electronic device, an information-related terminal, and a touch sensor device.
    - **9.** A method of making a substrate (100), the method comprising the steps of:
- a. providing a sheet comprising at least one of a glass, a glass ceramic, and a ceramic and having a first surface (102) and a second surface (104) that are substantially parallel to each other, and at least two parallel high strength edges between the first surface (102) and the second surface (104), wherein each of the at least two parallel edges has a bend strength capable of less than 2% failure probability at a stress level of 200 MPa over a test length of 50 mm; and
  - b. depositing a polymeric edge coating (120) on at least a portion of each of the at least two parallel high strength edges to form the substrate (100), wherein the polymeric edge coating (120) has a thickness in a range from 5  $\mu$ m to 50  $\mu$ m,

**characterised in that** each of the at least two parallel high strength edges is unfinished; **in that** the first surface (102) of the sheet and the second surface (104) of the sheet are each entirely free of the polymeric edge coating (120); and **in that** the polymeric edge coating (120) comprises at least one of a silicone, an epoxy, an acrylate, a urethane, and combinations thereof.

- **10.** The method according to Claim 9, wherein the step of providing the sheet comprises forming a sheet by one of fusion-drawing, slot-drawing, and redrawing.
- **11.** The method according to Claim 9 or Claim 10, wherein the step of cutting the sheet comprises laser cutting the sheet to form the at least two parallel high strength edges.

# 45 Patentansprüche

15

20

30

35

40

- 1. Substrat (100), wobei das Substrat (100) Folgendes umfasst:
- a. eine Platte, die zumindest eines von einem Glas, einer Keramik und einer Glaskeramik umfasst, wobei die Platte eine erste Oberfläche (102), eine zweite Oberfläche (104) und mindestens zwei parallele hochfeste Ränder, die die erste Oberfläche (102) und die zweite Oberfläche (104) zusammenfügen, aufweist, wobei jeder der mindestens zwei parallelen hochfesten Ränder eine Biegefestigkeit aufweist, die zu weniger als 2% Ausfallwahrscheinlichkeit bei einem Beanspruchungsniveau von 200 MPa über eine Testlänge von 50 mm fähig ist; und
  - b. eine Polymerrandbeschichtung (120), die zumindest einen Abschnitt von jedem der mindesten zwei parallelen hochfesten Ränder abdeckt, wobei die Polymerrandbeschichtung (120) eine Dicke in einem Bereich von 5  $\mu$ m bis 50  $\mu$ m aufweist und jeden der mindestens zwei parallelen hochfesten Ränder vor dem Einbringen von Defekten und Schaden schützt, **dadurch gekennzeichnet, dass** jeder der mindestens zwei parallelen hoch-

festen Ränder unfertig ist; dass die erste Oberfläche (102) der Platte und die zweite Oberfläche (104) der Platte jeweils vollständig frei von der Polymerrandbeschichtung (120) sind; und dass die Polymerrandbeschichtung (120) mindestens eines von einem Silikon, einem Epoxid, einem Akrylat, einem Urethan und Kombinationen davon umfasst.

5

- 2. Substrat (100) nach Anspruch 1, wobei das Substrat (100) eine Dicke von bis zu 0,6 mm aufweist.
- 3. Substrat (100) nach Anspruch 2, wobei das Substrat (100) eine Dicke von bis zu 0,1 mm aufweist.
- 4. Substrat (100) nach einem der Ansprüche 1-3, wobei die Polymerrandbeschichtung (120) ein Modul von bis zu 10 GPa aufweist.
  - 5. Substrat (100) nach einem der Ansprüche 1-4, wobei das Substrat (100) mindestens eine verstärkte Oberflächenschicht aufweist, die sich von mindestens einer der ersten Oberfläche (102) und der zweiten Oberfläche (104) zu einer Schichttiefe erstreckt, wobei die verstärkte Oberflächenschicht unter einer Druckbeanspruchung ist.
  - 6. Substrat (100) nach Anspruch 5, wobei die verstärkte Oberflächenschicht eine ionenausgetauschte Schicht ist.
  - 7. Substrat (100) nach einem der Ansprüche 1-6, ferner umfassend mindestens eine Schicht, die auf mindestens eine der ersten Oberfläche (102) und der zweiten Oberfläche (104) abgeschieden ist.
    - **8.** Substrat (100) nach einem der Ansprüche 1-7, wobei das Substrat (100) ein Schutzabdeckungsglas für mindestens eines von einem tragbaren elektronischen Gerät, einem informationsbezogenen Endgerät und einer Berührungssensorvorrichtung ist.

25

30

35

15

20

- 9. Verfahren zum Herstellen eines Substrats (100), wobei das Verfahren folgende Schritte umfasst:
  - a. Bereitstellen einer Platte, die zumindest eines von einem Glas, einer Glaskeramik und einer Keramik umfasst eine erste Oberfläche (102), eine zweite Oberfläche (104), die im Wesentlichen parallel zueinander sind, und mindestens zwei parallele hochfeste Ränder zwischen der ersten Oberfläche (102) und der zweiten Oberfläche (104) aufweist, wobei jeder der mindestens zwei parallelen Ränder eine Biegefestigkeit aufweist, die zu weniger als 2% Ausfallwahrscheinlichkeit bei einem Beanspruchungsniveau von 200 MPa über eine Testlänge von 50 mm fähig ist; und
  - b. Abscheiden einer Polymerrandbeschichtung (120), auf zumindest einen Abschnitt von jedem der mindestens zwei parallelen hochfesten Ränder, um das Substrat (100) zu bilden, wobei die Polymerrandbeschichtung (120) eine Dicke in einem Bereich von 5 µm bis 50 µm aufweist, **dadurch gekennzeichnet, dass** jeder der mindestens zwei parallelen hochfesten Ränder unfertig ist; dass die erste Oberfläche (102) der Platte und die zweite Oberfläche (104) der Platte jeweils vollständig frei von der Polymerrandbeschichtung (120) sind; und dass die Polymerrandbeschichtung (120) mindestens eines von einem Silikon, einem Epoxid, einem Akrylat, einem Urethan und Kombinationen davon umfasst.

40

- **10.** Verfahren nach Anspruch 9, wobei der Schritt des Bereitstellens der Platte das Bilden einer Platte durch eines von Schmelzziehen, Düsenziehen und Wiederziehen umfasst.
- **11.** Verfahren nach Anspruch 9 oder Anspruch 10, wobei der Schritt des Schneidens der Platte das Laserschneiden der Platte umfasst, um die mindestens zwei parallelen hochfesten Ränder zu bilden.

# Revendications

50

- 1. Substrat (100), le substrat (100) comprenant :
  - a. une feuille comprenant au moins un matériau parmi du verre, de la céramique et de la vitrocéramique, la feuille ayant une première surface (102), une seconde surface (104) et au moins deux bords hautement résistants parallèles reliant la première surface (102) à la seconde surface (104), chacun des au moins deux bords hautement résistants parallèles ayant une résistance à la flexion permettant une probabilité de défaillance inférieure à 2 % à un niveau de contrainte de 200 MPa sur une longueur d'essai de 50 mm ; et
    - b. un revêtement polymère de bord (120) recouvrant au moins une partie des chacun des au moins deux bords

hautement résistants parallèles, le revêtement polymère de bord (120) ayant une épaisseur dans la plage comprise entre 5  $\mu$ m et 50  $\mu$ m et protégeant chacun des au moins deux bords hautement résistants parallèles contre l'introduction de défauts et la détérioration,

- caractérisé en ce que chacun des au moins deux bords hautement résistants parallèles est non fini ; en ce que la première surface (102) de la feuille et la seconde surface (104) de la feuille sont chacune entièrement dépourvues de revêtement polymère de bord (120) ; et en ce que le revêtement polymère de bord (120) comprend au moins un matériau parmi du silicone, de l'époxy, de l'acrylate, de l'uréthane et leurs combinaisons.
- 10 2. Substrat (100) selon la revendication 1, le substrat (100) ayant une épaisseur de 0,6 mm maximum.
  - 3. Substrat (100) selon la revendication 2, le substrat (100) ayant une épaisseur de 0,1 mm maximum.
  - 4. Substrat (100) selon l'une quelconque des revendications 1 à 3, dans lequel le revêtement polymère de bord (120) a un module de 10 GPa maximum.
  - 5. Substrat (100) selon l'une quelconque des revendications 1 à 4, le substrat (100) présentant au moins une couche de surface renforcée qui s'étend à partir de la première surface (102) et/ou de la seconde surface (104) jusqu'à une profondeur de couche, la couche de surface renforcée étant soumise à une contrainte de compression.
  - **6.** Substrat (100) selon la revendication 5, dans lequel la couche de surface renforcée est une couche échangeuse d'ions.
  - 7. Substrat (100) selon l'une quelconque des revendications 1 à 6, comprenant en outre au moins une couche déposée sur la première surface (102) et/ou la seconde surface (104).
    - 8. Substrat (100) selon l'une quelconque des revendications 1 à 7, le substrat (100) étant un verre de protection pour au moins un dispositif parmi un dispositif électronique portatif, un terminal d'informations et un dispositif de détection tactile.
    - 9. Procédé de réalisation d'un substrat (100), le procédé comprenant les étapes suivantes :
      - a. la fourniture d'une feuille comprenant au moins un matériau parmi du verre, de la vitrocéramique et de la céramique et présentant une première surface (102) et une seconde surface (104) qui sont sensiblement parallèles l'une à l'autre, et au moins deux bords hautement résistants parallèles entre la première surface (102) et la seconde surface (104), chacun des au moins deux bords parallèles ayant une résistance à la flexion permettant une probabilité de défaillance inférieure à 2 % à un niveau de contrainte de 200 MPa sur une longueur d'essai de 50 mm; et
      - b. le dépôt d'un revêtement polymère de bord (120) sur au moins une partie de chacun des au moins deux bords hautement résistants parallèles pour former le substrat (100), le revêtement polymère de bord (120) ayant une épaisseur dans une plage comprise entre 5  $\mu$ m et 50  $\mu$ m,
      - caractérisé en ce que chacun des au moins deux bords hautement résistants parallèles est non fini ; en ce que la première surface (102) de la feuille et la seconde surface (104) de la feuille sont chacune entièrement dépourvues de revêtement polymère de bord (120) ; et en ce que le revêtement polymère de bord (120) comprend au moins un matériau parmi du silicone, de l'époxy, de l'acrylate, de l'uréthane et leurs combinaisons.
    - **10.** Procédé selon la revendication 9, dans lequel l'étape de fourniture de la feuille comprend la formation d'une feuille par une des méthodes parmi l'étirage en fusion, l'étirage par fentes et le ré-étirage.
    - **11.** Procédé selon la revendication 9 ou la revendication 10, dans lequel l'étape de découpe de la feuille comprend la découpe au laser de la feuille pour former les au moins deux bords hautement résistants parallèles.

55

15

20

25

30

35

40

45

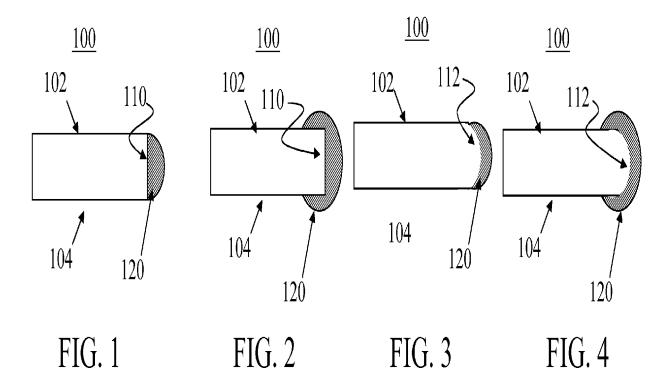
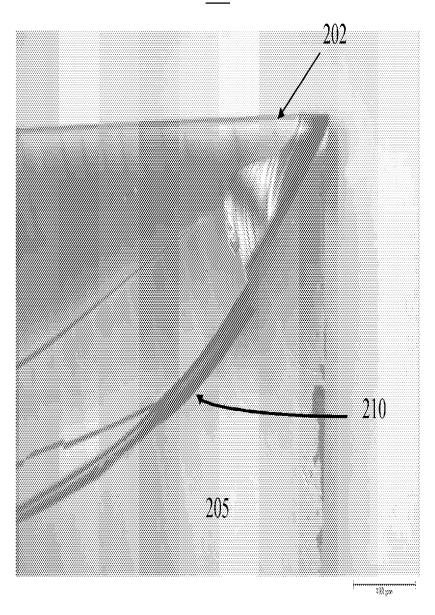


FIG. 5

<u>200</u>



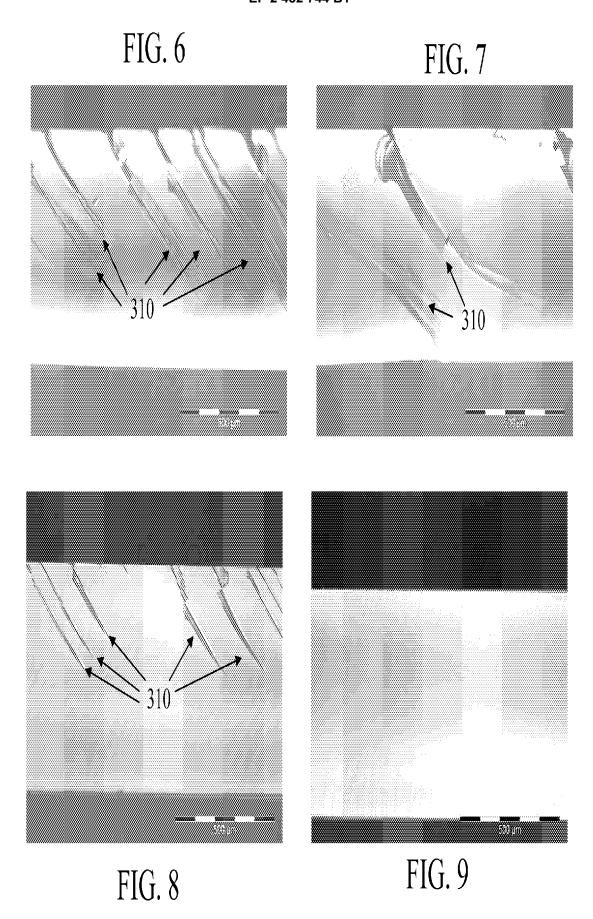
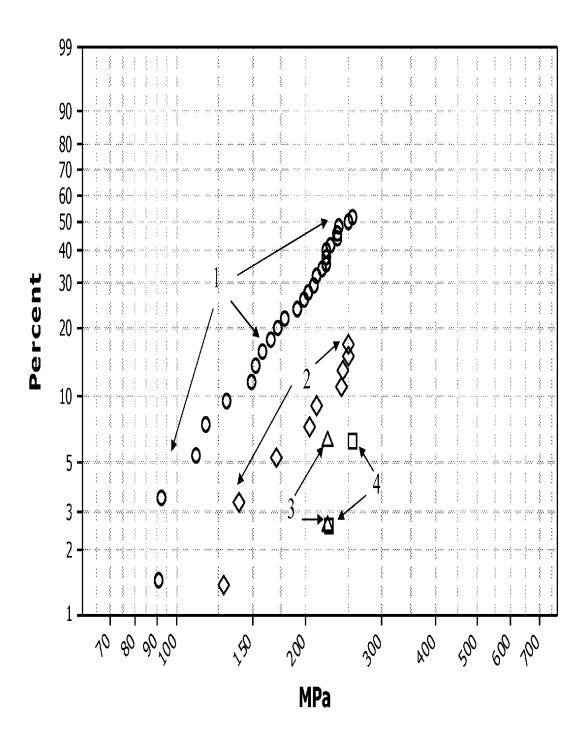


FIG. 10



# REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

# Patent documents cited in the description

- US 6815070 B1 [0002]
- DE 19810325 A1 [0002]
- WO 2007140978 A1 **[0002]**
- US 6120908 A [0002]
- US 46979409, Sean M. Garner [0027]
- US 12388935 B, Anatoli A. Abramov [0027]
- US 3986997 A, Howard A. Clark [0029]
- US 88821307, Adam J. Ellison [0037]
- US 93080807 [0037]

- US 27757308, Matthew J. Dejneka [0037]
- US 61004677 [0037]
- US 39257709, Matthew J. Dejneka [0037]
- US 61067130 [0037]
- US 39324109, Matthew J. Dejneka [0037]
- US 61067732 [0037]
- US 61087324, Kristen L. Barefoot [0037]
- US 61079995, Douglas C. Allan [0040]
- US 61084398, Christopher M. Lee [0040]